

DEPARTMENT OF COMMERCE

SCIENTIFIC PAPERS OF THE BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 387

PERMEABILITY OF RUBBER TO GASES

BY

JUNIUS DAVID EDWARDS, Associate Chemist

S. F. PICKERING, Associate Chemist

Bureau of Standards

JULY 12, 1920



20-26766

PRICE, 10 CENTS

Sold only by the Superintendent of Documents, Government Printing Office
Washington, D. C.

WASHINGTON
GOVERNMENT PRINTING OFFICE
1920

111102508

DEPARTMENT OF COMMERCE

SCIENTIFIC PAPERS
OF THE
BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 387

PERMEABILITY OF RUBBER TO GASES

BY

JUNIUS DAVID EDWARDS, Associate Chemist

S. F. PICKERING, Associate Chemist

Bureau of Standards

JULY 12, 1920



PRICE, 10 CENTS

Sold only by the Superintendent of Documents, Government Printing Office
Washington, D. C.

WASHINGTON
GOVERNMENT PRINTING OFFICE

1920

TS1892
E4

D. of D.
SEP 23 1920

31

20-26766

02/7/01 P. 327

PERMEABILITY OF RUBBER TO GASES

By Junius David Edwards and S. F. Pickering

CONTENTS

| | Page |
|--|------|
| I. Introduction..... | 327 |
| II. Nature of permeability process..... | 328 |
| III. Methods of determining permeability and characteristics of rubber samples employed..... | 328 |
| 1. Methods..... | 329 |
| 2. Characteristics of rubber samples employed..... | 330 |
| IV. Relation of permeability to composition of rubber..... | 332 |
| V. Relation of permeability to experimental conditions..... | 338 |
| 1. Relation of permeability to pressure..... | 338 |
| 2. Relation of thickness of rubber to permeability..... | 342 |
| 3. Time of penetration of rubber..... | 344 |
| 4. Relation of permeability to temperature..... | 345 |
| VI. Permeability of rubber to various gases..... | 347 |
| 1. Permeability of rubber to hydrogen..... | 347 |
| 2. Permeability of rubber to oxygen..... | 348 |
| 3. Permeability of rubber to nitrogen..... | 349 |
| 4. Permeability of rubber to argon..... | 350 |
| 5. Permeability of rubber to air..... | 350 |
| 6. Permeability of rubber to carbon dioxide..... | 351 |
| 7. Permeability of rubber to helium..... | 352 |
| 8. Permeability of rubber to ammonia..... | 354 |
| 9. Permeability of rubber to ethyl chloride..... | 356 |
| 10. Permeability of rubber to methyl chloride..... | 356 |
| 11. Permeability of rubber to water vapor..... | 357 |
| VII. Theory of permeability..... | 360 |
| VIII. Summary..... | 361 |

I. INTRODUCTION

Rubber has been in everyday use as a gas-retaining material for a great many years. Nevertheless, until the recent development of the modern rubberized balloon fabric, comparatively little advance was made in our knowledge of the permeability of rubber to gases. With the development of fabrics for lighter-than-air craft came the demand for accurate methods of measuring permeability, together with a demand for the most varied kinds of information regarding the permeability relations of rubber and gases. The Bureau of Standards has already, in its Technologic

Paper No. 113,¹ published the results of an investigation of methods for the determination of the permeability of rubber to hydrogen. The present investigation of the factors involved in the passage of gas through rubber and the permeability of rubber to different gases has been correlated with that work. The experimental work extended from 1917 to 1919; its publication has been delayed for obvious reasons.

II. NATURE OF PERMEABILITY PROCESS

Graham,² in his work on the "Dialytic Separation of Gases by Colloid Septa," was the first to point out that the characteristic passage of gas through rubber took place by solution in the rubber and not by diffusion through microscopic openings. If gases passed through rubber by the process of diffusion, as through a porous plate, their rates of penetration should be approximately inversely proportional to their viscosities. As pointed out by Graham, the relative rates of penetration of different gases bear no relation to their densities or viscosities. In fact, it is difficult to correlate the permeability with any of the well-known properties of the gases. It is quite obvious from a consideration of the facts that some phenomenon other than that of diffusion through small openings is concerned and that the properties of both rubber and gas determine the rate of penetration. Before entering on a discussion of this point the experimental facts which bear on the case will be presented.

III. METHODS OF DETERMINING PERMEABILITY AND CHARACTERISTICS OF RUBBER SAMPLES EMPLOYED

The permeability of a rubber film may be defined as the rate at which it is penetrated by a certain gas. Permeability will be expressed in terms of liters of gas per square meter per 24 hours, the volume of gas being corrected to the standard conditions of 0°C and 760 mm mercury pressure. Unless stated otherwise, all determinations are made under the following conditions, which are adopted as standard for this work: The fabric is held at a temperature of 25° C, with air at atmospheric pressure (760 mm of mercury) on one side of the fabric and the gas in question at an excess pressure of 30 mm of water on the other side.

¹ J. D. Edwards, Determination of Permeability of Balloon Fabrics, B. S. Tech. Paper No. 113; 1918.

² Phil. Mag., 32, p. 401; 1866.

1. METHODS

Most of the different types of apparatus available for the determination of permeability have been described in Technologic Paper No. 1113, to which reference has been made. Certain other apparatus developed recently will be mentioned in connection with the experimental work.

What may be called the standard apparatus of the Bureau of Standards is shown in diagram in Fig. 1. The rubber sample to be tested is held in the permeability cell *a*, which is maintained at a constant temperature in an air or water bath *h*. The cell consists of two circular plates with a shallow chamber in each. The test piece is held between the flanges of the cell and separates the

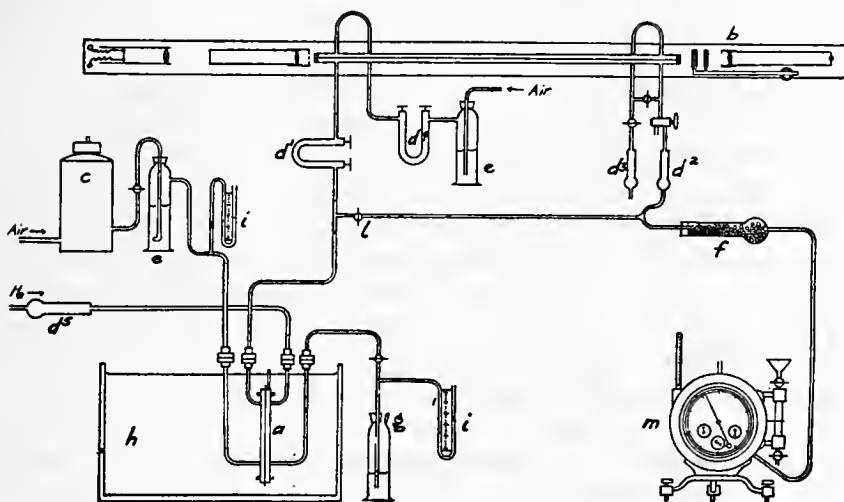


FIG. 1.—Standard apparatus for determining permeability of rubber to gases

two chambers; it is supported by a series of crossed wires in the form of a screen. A constant concentration of the gas whose permeability is to be measured is maintained in one chamber. The gas which penetrates the exposed area of rubber passes into the other chamber, from which it is continuously removed by a stream of air or other gas and determined quantitatively.

Because of the common use of hydrogen in balloons, the permeability to hydrogen is the property most often determined in the case of balloon fabrics. For this reason, and because of the accuracy with which the permeability to hydrogen can be determined, the permeability to any other gas will be referred to its permeability to hydrogen as the standard of comparison.

In determining the permeability to hydrogen a current of pure, dry hydrogen is passed over one side of the fabric and out through a water seal. Dry air under carefully regulated pressure is passed over the other side of the fabric through a drying tube d^1 and into one chamber of a gas interferometer, where the percentage of hydrogen in the air is determined optically. The gas then passes out through the drying tube d^2 , which prevents diffusion of water vapor into the interferometer, through the saturator f filled with glass beads partly covered with water, and then through the wet meter m . The saturator is employed to prevent loss of water from the meter by evaporation into the gas which is being measured. Arrangements are made for by-passing the air stream from the interferometer to the meter when the interferometer is being read and for supplying the comparison chamber of the interferometer with pure, dry air.

The gas interferometer³ of the Rayleigh type measures the difference in refractivity of the two samples of gas contained in the gas chambers of the instrument. Several interferometers were used, and their sensitivity was such that each scale division indicated from 0.007 to 0.01 per cent hydrogen in air. The average of 10 settings of the instrument gave a reading which was good to somewhat better than 1 scale division; this gives ample precision in the determination of the hydrogen. The calibration of the interferometer, both for hydrogen and other gases, was accomplished by the method described by one of the present authors in the *Journal of the American Chemical Society*.⁴ By the use of this method the utility of the interferometer was greatly extended, and we were enabled to handle accurately such mixtures as helium and air, which are difficult to analyze by other methods. The interferometer furnishes a rapid and accurate means of analyzing many gas mixtures, and its use will be discussed further in that connection in this paper.

2. CHARACTERISTICS OF RUBBER SAMPLES EMPLOYED

The greater part of the determinations recorded were made with rubber films as they are contained in balloon fabrics. This was done not only because of the immediate application of the results in that field, but also because balloon fabrics of great variety were readily available. Rubber films of satisfactory uniformity and low permeability are also most easily secured in the form of balloon

³ For detailed description see L. H. Adams, *J. Am. Chem. Soc.*, **37**, p. 1181; 1915.

⁴ Edwards, *J. Am. Chem. Soc.*, **39**, p. 2382; 1917.

fabrics. The support given the rubber film by the cloth on which it is spread simplifies the handling and testing of the material. The question might be raised as to whether in some cases the results might not be influenced by the cloth on which the rubber is spread. To test this point, determinations were also made on thin sheet rubber in those instances. The absolute permeability of the rubber is profoundly modified by the cloth, as will be shown later; its relative permeability to different gases is apparently not affected thereby.

The presence of the cloth, however, introduces a factor which may lead to serious errors in testing if not properly taken account of. Most balloon fabrics are constructed of two plies of cloth with a film of rubber between the plies and a thinner coating of rubber on the inside and outside for the purpose of protection; these inner and outer coatings have little effect in reducing the permeability of the fabric. The rubber does not penetrate very thoroughly into the interstices between the threads, and, as a result, hydrogen is able to diffuse laterally along the cloth as well as directly through the rubber film. Hydrogen can therefore diffuse along the textile and into the area clamped between the edges of the cell which, it might be assumed, is not active in the test. Here it can pass through the main layer of rubber, back through the textile on the other side, and into the air chamber. The exposed or "active" area of fabric is, then, larger than the area defined by the edges of the cell, and the results are correspondingly high. If there be no rubber on either side or only on one side, the interstices in the cloth can be satisfactorily sealed with vaseline or soft wax applied hot, which fills up the openings between the threads and prevents lateral diffusion of the hydrogen. If the fabric has a rubber coating on both sides, the vaseline can not penetrate this rubber into the cloth underneath; no satisfactory method of sealing such fabrics is available. The best procedure in that case, is to reduce the margin of the fabric to as small an area as possible and put hot wax on the edge. The possible error, if the whole margin is active, can then be estimated.

The "edge effect" can be illustrated by the results of a series of experiments on limiting the area of a test piece (see Table 1). Two samples of two-ply fabric were tested, one having an outside rubber coating on one side only and the other being rubber coated on both sides. The total area of each test piece was about 130

cm², but the exposed area was reduced to 100, 90, and 70 cm² by coating with grease. With the fabric having one cloth surface it is seen that the area is accurately defined in each test. With the fabric having rubber on both surfaces, practically the whole area of the test piece is effective.

TABLE 1.—Effect of Limiting Area of Test Piece

| Description of fabric | Apparent permeability—Liters; exposed area ^a limited to— | | |
|---|---|--------------------|--------------------|
| | 100 cm ² | 90 cm ² | 70 cm ² |
| Rubber coat on one side only of two-ply fabric..... | 12.1 | 12.2 | 12.1 |
| Rubber coat on both sides of two-ply fabric..... | 11.8 | 15.8 | 16.6 |

^aThe exposed area was used in calculating the permeability per square meter.

The fabric (No. 50313) with which a great deal of the experimental data were obtained in succeeding experiments was a two-ply fabric without rubber coating on either side. Where it was necessary for some reason or other to use fabrics having rubber on both sides, the edge effect was made as small as possible by reducing the margin to a minimum; its effect on the relative values of tests was then without significance.

IV. RELATION OF PERMEABILITY TO COMPOSITION OF RUBBER

Crude rubber, as well as vulcanized rubber, may vary so widely in composition and physical characteristics that one can hardly expect to find or define such a constant as the specific permeability of rubber. Part of the disagreement between previous experimenters has been ascribed to differences in the samples of rubber which were tested. Nevertheless, certain regularity of behavior has been noted and certain observations made on the relation between permeability and composition which are of interest and value.

For the present purpose rubber may be considered to be a mixture of "polyprene" (C₈H₈)_x in different stages of polymerization, together with resins, nitrogenous matter, water, and inorganic material in varying proportions. Vulcanized rubber, which we will hereinafter refer to simply as rubber, contains, in addition, varying proportions of sulphur, combined with or adsorbed by the polyprene, together with some free sulphur. Compounding materials in great variety may also be added to the rubber to

give it desirable characteristics, but where imperviousness to gases is desired their use is usually restricted.

The effect of sulphur upon permeability may be considered in connection with the effect of vulcanization, since the two factors are interrelated. The effect of different degrees of vulcanization or "cure" upon permeability is shown, for one compound, by the series of tests given in Table 2. The samples were taken from a roll of two-ply balloon fabric, different sections of which had been given different degree of vulcanization, as indicated. Except for variations in the uniformity of spreading, the temperature and time of heating were the only variables.

TABLE 2.—Effect of Time and Temperature of Vulcanization Upon Permeability^a

| Sample No. | Vulcanization (steam heat) | | Sulphur | | Acetone extract (sulphur free) | Permea- bility |
|------------|-------------------------------|-------|---------------|----------|---|-------------------|
| | | | Com- bined | Free | | |
| | Hours | ° F | Per cent | Per cent | | Liters |
| 37010..... | None | | 0.3 | 4.3 | 3.8 | 12.8 |
| 37009..... | 0.5 | 270 | .5 | 3.2 | 3.2 | 11.6 |
| 37008..... | 1.0 | 270 | 1.4 | 2.5 | 3.2 | 11.5 |
| 37005..... | 1.0 | 284 | 1.3 | 1.8 | 3.0 | 12.7 |
| 37007..... | 1.25 | 284 | 1.6 | 2.1 | 3.0 | 15.5 |
| 37004..... | 1.0 | 288 | 2.5 | 2.1 | 3.2 | 12.2 |
| 37006..... | 1.5 | 284 | 2.3 | 1.8 | 3.0 | 12.8 |

^a The chemical analysis was made about eight months after the permeability determinations. The free sulphur may, therefore, be somewhat lower than that originally present.

This series of fabrics shows no significant variation in permeability which can not be ascribed to lack of complete uniformity in the fabric. The combined sulphur varied from practically nothing to 2.5 per cent.

In a similar series of tests samples were taken from adjacent portions of 13 different rolls of fabric before and after vulcanization. In two cases the permeability was the same before and after vulcanization; in five cases the permeability of the uncured sample was the highest and in the remaining six cases the reverse was true. The average difference was only 1 liter. The average combined sulphur before and after vulcanization was 0.76 and 1.07 per cent, respectively; similarly the average acetone extract was 3.8 and 3.7 per cent.

In Table 3 are shown the results of another series of tests in which the time and temperature of vulcanization were varied. The permeability and chemical characteristics are given both for

the fabric as received and after storage under ideal conditions (in a cool, dark place) for 12 months. It may be remarked, to begin

TABLE 3.—Relation of Composition to Permeability^a

| Sample No. | Time and temperature of cure | | Composition and permeability as received | | | | Composition and permeability after storage (12 months) | | | |
|------------|------------------------------|-----|--|--------------|------------------|--------------|--|--------------|------------------|--------------|
| | | | Acetone extract | Free sulphur | Combined sulphur | Permeability | Acetone extract | Free sulphur | Combined sulphur | Permeability |
| | Hours | ° F | Percent | Percent | Percent | Liters | Percent | Percent | Percent | Liters |
| 27003..... | 3 | 270 | 3.1 | 2.9 | 1.6 | 23.5 | 5.4 | 2.2 | 1.6 | 17.7 |
| 27000..... | 4 | 270 | 5.1 | 3.0 | 1.9 | 20.4 | 6.0 | 3.2 | 2.6 | 18.8 |
| 27002..... | 3 | 290 | 5.2 | .9 | 3.7 | 18.8 | 6.3 | .7 | 4.1 | 13.2 |
| 27001..... | 4 | 290 | 5.3 | 1.1 | 4.0 | 15.8 | 7.6 | .6 | 4.7 | 9.5 |
| 26998..... | 3 | 270 | 6.1 | 5.7 | 1.8 | 20.6 | 5.9 | 3.6 | 3.6 | 15.4 |
| 26997..... | 4 | 270 | 5.7 | 4.4 | 2.0 | 19.9 | 4.2 | 4.6 | 2.9 | 14.9 |
| 26999..... | 3 | 290 | 5.5 | 1.7 | 3.6 | 16.8 | 12.0 | .6 | 5.2 | 4.0 |
| 26996..... | 4 | 290 | 5.8 | 1.9 | 4.8 | 14.9 | 16.8 | .5 | 6.3 | 6.0 |
| 26995..... | 4 | 270 | 5.8 | 4.9 | 2.1 | 23.8 | 5.3 | 3.5 | 2.8 | 14.0 |
| 26994..... | 4 | 290 | 6.9 | 1.6 | 4.6 | 15.9 | 13.6 | .5 | 5.7 | 2.4 |
| 26992..... | 4 | 270 | 5.3 | 3.8 | 1.7 | 20.5 | 16.6 | .4 | 6.8 | 6.8 |
| 26993..... | 4 | 290 | 6.3 | 1.7 | 5.0 | 10.6 | 17.7 | .5 | 8.0 | 1.3 |

^a All fabrics were two-ply construction. They varied in weight and distribution of rubber compound. The percentage of sulphur was varied in two different proportions, but this was the only change in the composition of the rubber compound. Fabrics grouped together were of identical construction except for variations in cure. The analyses were calculated on the basis of the rubber compound contained and not on the weight of rubber plus fabric.

with, that practically all of these fabrics were somewhat over-cured. The rubber had the characteristic odor of overcured balloon fabric, and many of the samples became quite stiff with time; some reached the stage where the rubber compound was brittle and cracked on bending. The most noticeable facts which these results show are that with these fabrics the permeability decreased during storage and that there was a concomitant increase of combined sulphur and acetone extract. If the percentages of combined sulphur are plotted as abscissæ and the permeabilities as ordinates, the graph shown in Fig. 2 is obtained. As shown by the legend, data on fabrics which have been exposed outdoors for 30 days are also included. There apparently is some relation in this series between the permeability and the percentage of combined sulphur. The acetone extract also increases at the same time, but there is no such striking relation between these two variables as that shown in Fig. 2. The original acetone extract is about the same on all the fabrics, but the permeability shows a considerable variation.

Similar decreases in permeability are observed when fabrics are exposed to the weather. In Fig. 3 are shown the relations between permeability and period of exposure for three different fabrics. The periods of testing were not frequent enough to locate the lowest point on each curve, but the curves indicate that the permeability reaches very low values. This lower permeability is accompanied

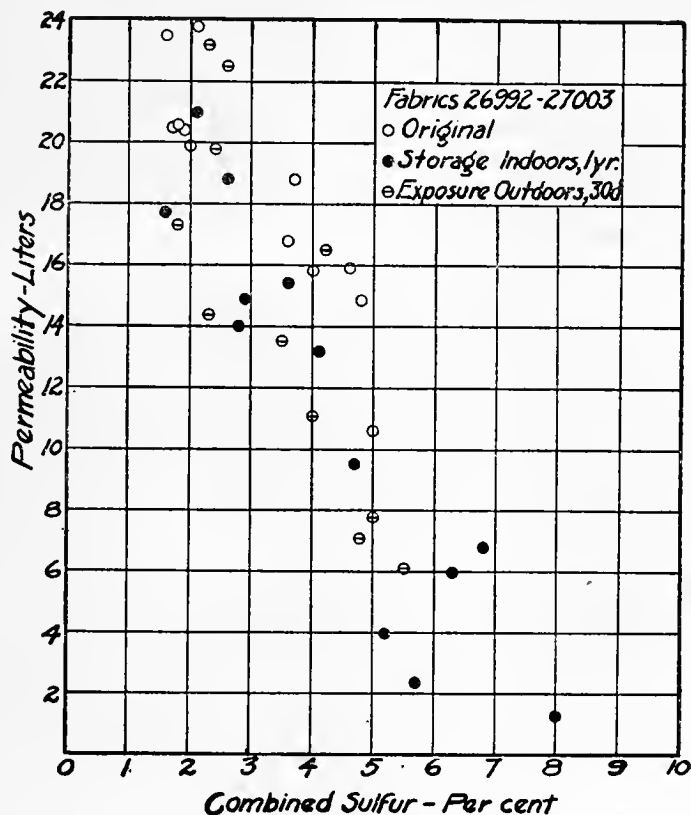


FIG. 2.—Graph showing decrease in permeability of rubber with increase of combined sulphur

by a characteristic hardening of the rubber. When the rubber film becomes sufficiently brittle it cracks easily and thereafter shows a very high permeability. The changes in permeability shown by the graphs were accompanied by the following changes in chemical characteristics at the time the lowest permeability was observed.

TABLE 4.—Change in Chemical Characteristics of Rubber in Three Fabrics of Fig. 3

| Composition | Fabric No. 10650 | | Fabric No. 10652 | | Fabric No. 23990 | |
|-----------------------|------------------|-----------------|------------------|-----------------|------------------|-----------------|
| | Original | 45 days | Original | 60 days | Original | 150 days |
| Combined sulphur..... | Per cent 1.4 | Per cent 1.7 | Per cent 3.0 | Per cent 4.2 | Per cent 1.5 | Per cent 2.5 |
| Free sulphur..... | .5 | .2 | 2.8 | .2 | 1.2 | .2 |
| Acetone extract..... | 3.1 | 50.0 | 3.2 | 16.2 | 4.0 | 42.9 |

In the case of fabrics exposed outdoors there is sometimes an increase in permeability during the initial period of exposure, which is followed later by the customary decrease. This increase is not accompanied, apparently, by any significant change in chemical characteristics.

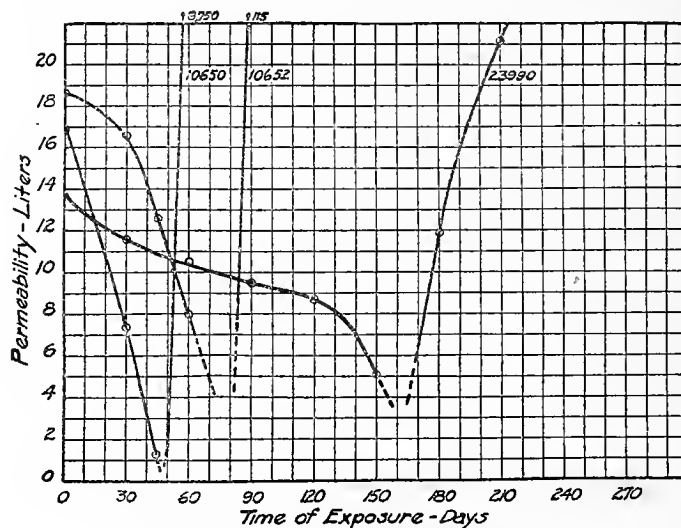


FIG. 3.—Effect upon permeability of exposure of rubber to the weather

Preliminary to drawing any conclusions from them it may be desirable to summarize the observed facts in regard to permeability and composition as shown by the preceding tests.

1. The aging of rubber in thin films is accompanied by a characteristic decrease in permeability.
2. The aging of rubber is usually accompanied by a decrease in the percentage of total sulphur; the combined sulphur increases by varying amounts and the free sulphur decreases eventually to a low value.

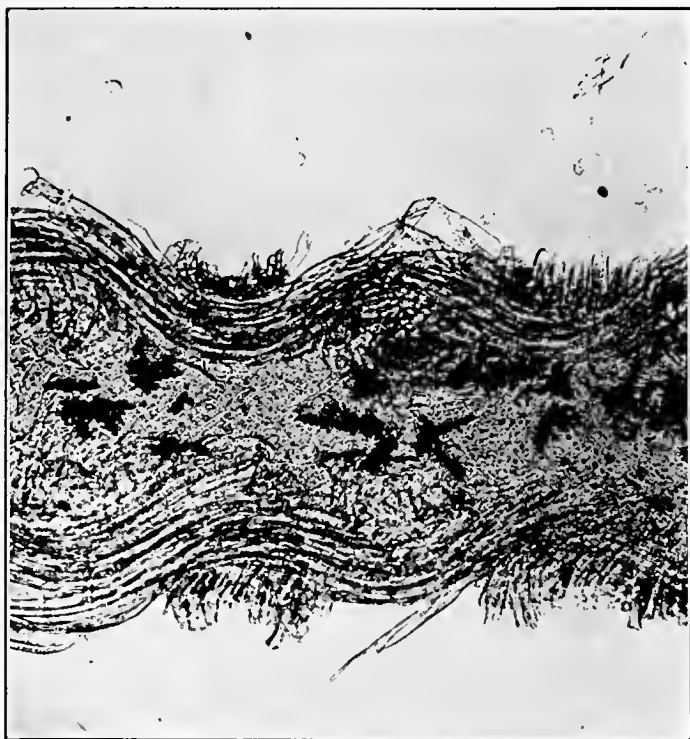


FIG. 4.—Section of balloon fabric, showing crystals of sulphur. ($\times 138$)



3. In one series of fabrics where the degree of cure was varied no significant change in permeability was observed. In this case the percentage of combined sulphur varied from 0.3 to 2.5 per cent. In another series large changes in permeability were noted with change in the degree of cure; the combined sulphur varied from 1.6 to 5 per cent. The original acetone extract was approximately constant in each series.

Because of the number of factors involved and because of the relatively small number of data presented, it would be unwise to draw any very extensive conclusions. The view is quite widely held by manufacturers and others that the permeability of a fabric can be reduced by increasing the degree of cure. Between certain limits this is true. That this reduction in permeability is caused entirely by the increase in combined sulphur is not at all certain. Opposed to this latter view is the fact that as great and greater decreases in permeability are noted on exposed fabrics where there are relatively small changes in combined sulphur. (See Fig. 3 and Table 4.) The most striking change in exposed fabrics is the increase in acetone extract, which increase is a measure of the resinification and oxidation of the rubber. It appears reasonable to believe, therefore, that an increase in both the combined sulphur and acetone extract causes a decrease in permeability. This would be the natural result if hydrogen was insoluble in both the acetone-soluble material and the "polyprene sulphide."

It has been thought by some that the free sulphur plays an important part in determining the permeability. The free sulphur which is present in the colloidal condition in the rubber after vulcanization frequently crystallizes out. This is strikingly shown by the microsection of a sample of ballonnet fabric illustrated in Fig. 4. The sulphur crystals are seen as dark dendritic masses in the rubber between the two plies of cloth. A certain amount of this sulphur eventually penetrates to the surface and evaporates. This process might possibly produce a certain porosity which would increase the permeability. Tests made on portions of the fabric of Fig. 4, where crystallization was extensive, showed no significant difference in permeability as compared with portions where crystallization had not occurred. Certainly our tests and experimental methods have not been of sufficient delicacy to detect any effect on the permeability which can be ascribed to this blooming out of sulphur.

Compounding materials may be added to the rubber either to make it more impervious to gases or to give it greater durability. Paraffin and glue are two substances which are said to lower the permeability of rubber to hydrogen. It is known that either of them alone will give a film of very low permeability, provided it is nonporous. Their use is not essential, however, to the production of a satisfactory coating for balloon fabrics. Lampblack, zinc oxide, or litharge may be incorporated in the rubber to give it greater life by protecting the rubber from the injurious action of light. No systematic investigation of the effect of these substances has been undertaken; our work has been confined almost exclusively to rubber compounds of the simplest composition.

V. RELATION OF PERMEABILITY TO EXPERIMENTAL CONDITIONS

1. RELATION OF PERMEABILITY TO PRESSURE

In considering the effect of pressure, a distinction should be made between the total pressure and the partial pressure of any constituent. A difference in the total pressure on the two sides will produce tension in the rubber film and a change in thickness or physical properties may result. The effect of a change in the total pressure will be influenced by the support given the rubber film, such as when it is held between cloth of one or more plies, as in the case of a balloon fabric.

The work of previous investigators indicates that the permeability of rubber to any gas is about proportional to the partial pressure of that gas. The agreement on this point is not unanimous, however, and the methods and data recorded are not satisfactory in all particulars. Almost all of the recorded measurements were made with apparatus of the volume-loss type; that is, they measured the loss in volume of a mass of gas confined by the rubber. The diffusion took place under varying pressure, and the back diffusion of air was seldom corrected for. In some cases the total pressure and partial pressure varied simultaneously, a condition which is obviously undesirable.

In Fig. 5 is shown the relation between permeability and difference in partial pressure of hydrogen, as shown by tests on six different test pieces of the same fabric. The percentages of hydrogen in the air were determined by means of the interferometer. The permeability of the different test pieces with 100 per cent hydrogen varied from 9.4 to 10 liters; each result was,

therefore, multiplied by the ratio of 10 to the observed permeability at 100 per cent, so that the 100 per cent value became 10 in each case and all the other values were directly comparable. It may be concluded from these results that the permeability is directly proportional to the partial pressure, within the limits of experimental error.

Similar results were obtained with carbon dioxide, as shown in Fig. 6. In addition to the balloon fabric (No. 50313) a sample of thin rubber known as "dental dam" was also tested. The permeability in each case was directly proportional to the partial pressure, any deviation being reasonably ascribed to experimental error. The values indicated for fabric No. 50313 are the averages of tests on seven different test pieces. To make the results

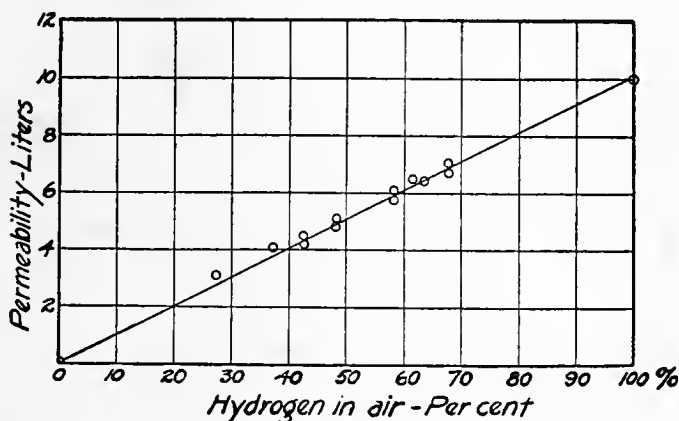


FIG. 5.—Relation between permeability and partial pressure of hydrogen

directly comparable and save plotting a graph for each of the seven test pieces, the results were corrected, as in the case of the experiments with hydrogen, by reducing the 100 per cent values to the same figure by direct proportion and changing the other values proportionally.

In accordance with the conclusion that the permeability was directly proportional to the partial pressure, the results of all permeability determinations have been corrected to the standard condition of a partial pressure of 760 mm in the following manner: In one determination with carbon dioxide (99.9 per cent pure) there was 0.6 per cent carbon dioxide in the air on the opposite side of the fabric; the barometric pressure was 750 mm and the observed permeability 20 liters. The corrected permeability is then equal to $20.0 \times \frac{760}{750} \times \frac{100.0}{99.9 - 0.6}$, or 20.4 liters.

The change in permeability when the difference in the total pressure on the two sides of the sample is varied follows no simple law. In this case, not only does the permeability change with the change in partial pressure, but also it may change with any variation in thickness caused by the tension on the rubber. Obviously, the effect will vary with the support given the rubber. In the case of a balloon fabric the rubber film is given very intimate support by the cloth on which it is spread. The cloth may to some extent be prevented from stretching by the manner in

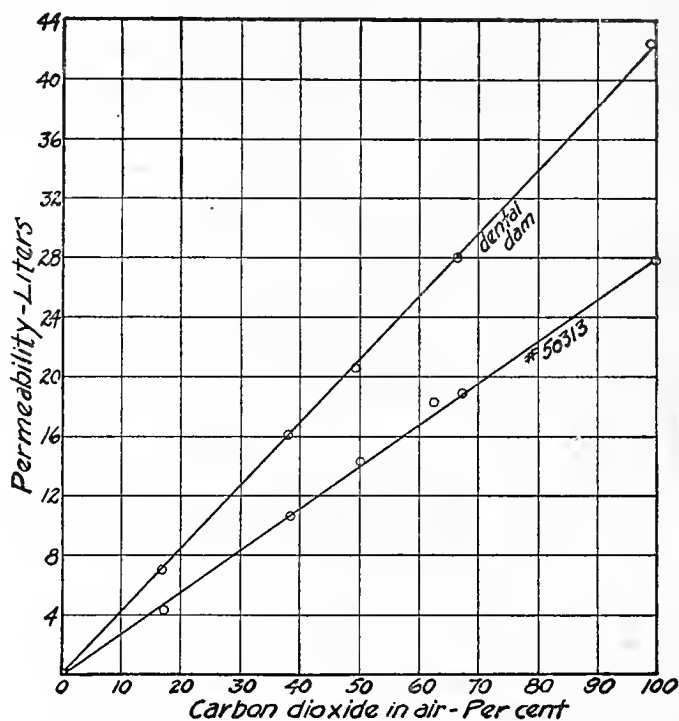


FIG. 6.—Relation between permeability and partial pressure of carbon dioxide

which it is held in the cell during a test. In the case of a sheet of rubber such as dental dam, the only support the rubber receives is from the screen on which it rests in the cell and the fact that it is clamped at the edges. In Fig. 7 are shown the graphs of several experiments where the pressure of the hydrogen was varied. Four different pieces of fabric No. 50313 were tested, and, to make the results more nearly comparable in the graph, the values were reduced by direct proportion, so that the values at 100 mm were identical; the 100 mm point, therefore, repre-

sents four determinations. The two balloon fabrics (Nos. 50313 and 47174) show about the same small rate of increase of permeability with increase of pressure. The two samples of dental dam show a slightly higher rate. The sample of dental dam showing the higher permeability was supported in the cell during the test by a screen having openings 4 cm^2 in area; the other sample was supported by wire gauze of 28 mesh. At least part of the difference in permeability can be ascribed to the greater stretching of the rubber in the case of the first sample mentioned. The extensibility of rubber and cloth may vary so greatly that no

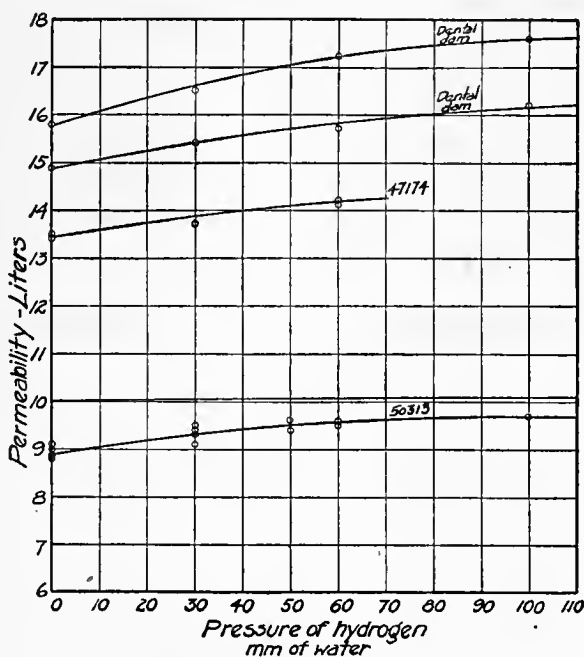


FIG. 7.—Relation between permeability and total pressure of hydrogen

great uniformity in the shape of these curves can be expected, and, in general, that is our experience. However, the rate of increase of permeability is much smaller above than below 60 mm in every case. For the sake of comparison, there is included the graph showing the change in permeability of a 10-liter fabric, which would be caused by the increase in partial pressure of the hydrogen; this increase is only 0.1 liter in the range from 0 to 100 mm of water pressure. The slopes of the curves of Fig. 7 are a little lower than those shown in Technologic Paper No. 113 (p. 14) for the same relation.

2. RELATION OF THICKNESS OF RUBBER TO PERMEABILITY

The permeability of a sample of rubber should obviously bear some relation to the thickness of the material. The most reasonable assumption, and the one usually made, is that the permeability is inversely proportional to the thickness of the rubber. A series of samples of rubber, identical in chemical composition and physical properties, but differing in thickness, was not available for testing this point. It was necessary, therefore, to use material from different sources and varying in composition. The samples tested varied from the thin sheet rubber known as dental dam, about 0.2 mm in thickness, up to sheets of 2 mm thickness. Certain of the samples were "vapor cured" with sulphur chloride and the rest steam cured in the usual manner. Their chemical characteristics are shown in Table 5. The permeability of these samples was determined with zero difference of pressure on the two sides of the samples in order not to introduce any variation in the tests because of stretching of the material.

TABLE 5.—Chemical Characteristics of Rubber Samples of Fig. 8

| Sample No. | Thick-ness | Acetone extract | Com-bined sulphur | Free sulphur | Sample No. | Thick-ness | Acetone extract | Com-bined sulphur | Free sulphur |
|------------|------------|-----------------|-------------------|--------------|------------|------------|-----------------|-------------------|--------------|
| | Mm | Per cent | Per cent | Per cent | | Mm | Per cent | Per cent | Per cent |
| 1..... | 0.18 | 2.7 | 0.8 | 0.1 | 11..... | 0.66 | 2.7 | 2.4 | 2.6 |
| 2..... | .21 | 2.9 | 2.8 | .2 | 12..... | .74 | 2.3 | 2.9 | 1.9 |
| 3..... | .22 | 2.8 | .8 | .1 | 13..... | .76 | 3.7 | 3.8 | 1.7 |
| 4..... | .25 | 3.3 | 1.3 | .7 | 14..... | .81 | 2.8 | 2.5 | 2.1 |
| 5..... | .25 | 2.8 | 2.4 | .2 | 15..... | .86 | 2.7 | 3.0 | 2.2 |
| 6..... | .26 | 4.1 | .8 | .3 | 16..... | .89 | 3.1 | 3.5 | 1.4 |
| 7..... | .48 | 2.6 | 2.0 | 3.1 | 17..... | .90 | 15.4 | 4.9 | .5 |
| 8..... | .53 | 3.6 | 3.2 | 1.4 | 18..... | 1.93 | 3.5 | 3.8 | 1.1 |
| 9..... | .53 | 3.1 | 2.9 | 2.0 | 19..... | 2.00 | 4.9 | 4.2 | 2.6 |
| 10..... | .60 | 2.2 | 1.8 | .2 | 20..... | 2.20 | 3.4 | 2.9 | .2 |

Their permeability was determined with a Shakespere permeameter which was furnished to us by Prof. Shakespere, of Birmingham University. For descriptions of this apparatus and method the reader is referred to Reports of the British Advisory Committee for Aeronautics for the last two years, which will undoubtedly be made available eventually. The calibration of the permeameter has not been established to our entire satisfaction; the absolute values it gives are, however, in substantial agreement (about 10 per cent) with those obtained by the method of the Bureau of Standards. The instrument gives reproducible results of good precision for purposes of comparison.

The results of these tests are shown in Fig. 8, where the gas impedance, by which term the reciprocal of the permeability is designated, is plotted as a function of the thickness. There is clearly a linear relation between the two variables over a considerable range. Such uniformity as was found was hardly expected, considering the fact that the samples represented the product of a number of different makers and made no pretense of being uniform in composition. It will be noted that the very thin samples, about 0.2 to 0.3 mm in thickness, show a lower impedance (higher permeability) than corresponds to the straight line. This may possibly be due to the greater effect of nonuniformity in the very thin material. The sample 0.9 mm in thickness (No. 17), which

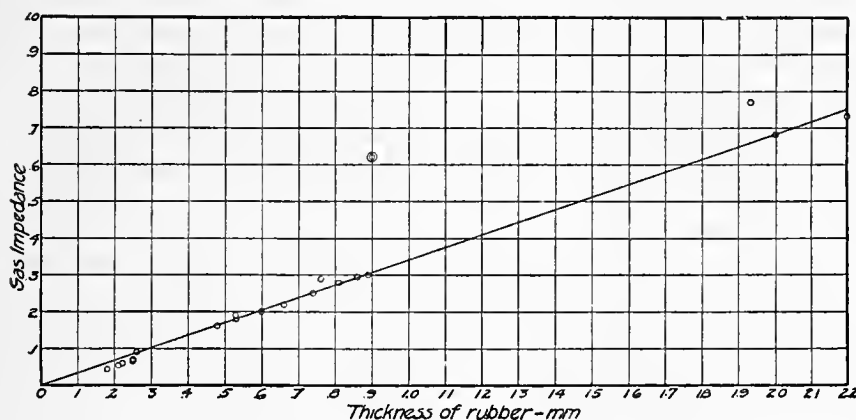


FIG. 8.—Relation between gas impedance (reciprocal of permeability) and thickness of rubber

showed an impedance of over 0.6, was old and stiff, and its high impedance was anticipated because of our observations on the decrease of permeability with age. This might also be inferred from its high acetone extract and combined sulphur values. The sample 1.93 mm in thickness contains glue which may account for its slightly greater impedance.

The results of Fig. 8 show sufficient uniformity to warrant calculating what may be called the specific permeability of rubber. It may be defined in terms analogous to those in which such a property as thermal conductivity is defined, by stating that it is the volume of gas which passes through unit area of a sample of unit thickness in unit time with a difference in partial pressure of 760 mm of the gas. The centimeter and minute can be conveniently used as units. The specific permeability

to hydrogen at 25° C of vulcanized rubber of the character described in Table 6, as calculated from the graph of Fig. 8, is 20.4×10^{-6} cc per minute. The volume of hydrogen passing through a sample of rubber at 25° C can be approximately calculated from the following equation:

$$V = \frac{20 \times 10^{-6} \times A \times t}{d}$$

where V is the volume in cubic centimeters, A the area in square centimeters, t the time in minutes, and d the thickness in centimeters.

The only other data in the literature which can be compared with the above value are those of Kayser.⁵ The specific permeability to hydrogen at 25° C as calculated from Kayser's equations is 27.4×10^{-6} cc per minute, which value is in fair agreement with ours. Although care should be taken not to place too great reliance on any value for the specific permeability of rubber the characteristics of which are unknown, nevertheless, the preceding equation will be found useful in arriving at an approximate figure in many cases. A direct permeability determination is the only sure method in any case.

The data of Fig. 8 confirm the very interesting observation of Prof. Shakespere that the gas impedance for a given weight of rubber is greatly increased by being spread on cloth. For example, a sheet of rubber (density, 0.96) having a weight of 120 g per square meter (about 3.5 ounces per square yard) will have a thickness of 0.13 mm and, according to Fig. 8, a permeability of $\frac{1}{0.042} = 23.8$ liters. This weight of rubber properly spread on cloth can be made to give a fabric having a permeability of about half that value, or 10 to 12 liters. The cloth, therefore, performs a very important function in reducing the permeability, in addition to giving the rubber support and protection. As pointed out by Prof. Shakespere, this fact is of importance in securing balloon fabrics of the lowest permeability.

3. TIME OF PENETRATION OF RUBBER

For some purposes, notably for use in gas masks, it is not the maximum permeability which is of most importance, but the time required for the gas to penetrate the fabric. A gas-mask fabric loses its protective value about as soon as the poison gas

⁵ Kayser, *Wied. Ann.*, 43, p. 544; 1891.

penetrates in appreciable quantities. Permeability determinations of the kind considered in the present work are, therefore, of very little value in this connection.

One test, made on a balloon fabric with the Shakespere permeameter, indicated that hydrogen penetrated the fabric in less than 1 minute and the fabric reached its maximum permeability in from 1 to 2 minutes. These times include the lag of the instrument, so that the actual time required to penetrate this fabric must be very small. The permeability of this fabric was about 8 liters per square meter per 24 hours. Tests made with hydrogen sulphide, in which the gas penetrating the rubber was detected with lead-acetate solution, showed that rubber films of the character used in balloon fabrics were penetrated with great rapidity by hydrogen sulphide also. Any considerable time required to reach equilibrium in testing may be generally considered to be caused by instrumental lag. Sometimes, however, there are actual changes in permeability with long-continued tests, which make it appear that equilibrium is being reached very slowly.

4. RELATION OF PERMEABILITY TO TEMPERATURE

Graham first called attention to the large temperature coefficient of permeability. The relation between temperature and permeability has been examined since then by a number of investigators, most of whom are in general agreement, although Frenzel's⁶ results alone indicate that the relation is a linear one. However, there are no reliable values which cover a very large range of temperatures.

A special cell was designed for determining the permeability at different temperatures. It was similar to the regular cell, except that each half was provided with a water jacket through which water could be circulated by means of a pump. By regulating the temperature of the water the fabric could easily be kept at any desired temperature within the range covered. The temperature of the fabric itself was measured by means of a copper-constantan thermocouple of No. 36 wire whose "hot junction" was mounted on the fabric before assembling the cell.

The results of measurements with hydrogen, helium, and carbon dioxide are assembled in Table 7. Because of possible, if not probable, changes in the rubber caused by heating or cooling,

⁶ Frenzel, "Über die Gasdurchlässigkeit der Ballonstoffe." Druckerei des Elsassischen Textiblattes in Gebweiler.

it was not considered advisable to use the same sample for each test. Therefore, in every test a determination was made at 25°C for purposes of comparison.

For graphic comparison the relative permeabilities are shown in Fig. 9. These curves are plotted from the data of Table 6,

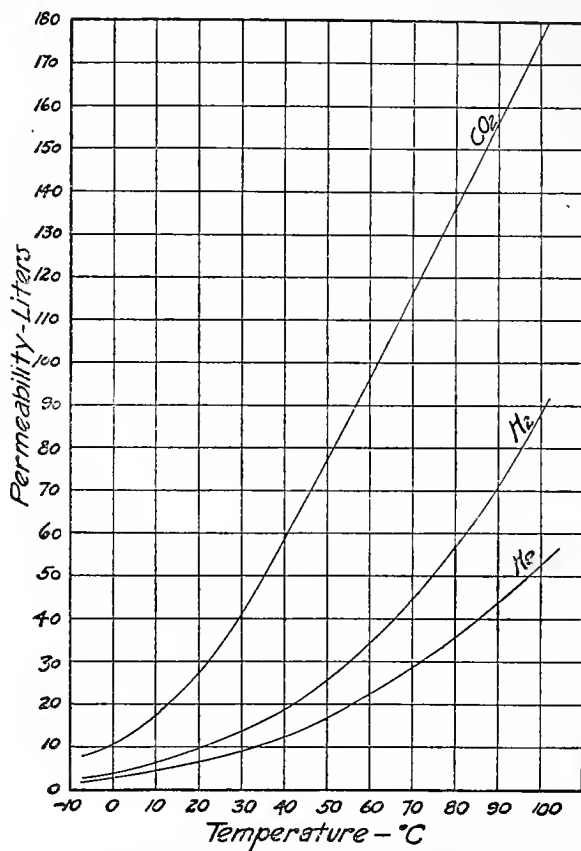


FIG. 9.—Relation between permeability and temperature for carbon dioxide, hydrogen, and helium

but the values have been adjusted proportionally to correspond to the same constant value at 25°C . The ratios of the permeabilities at 25°C have been chosen to correspond to the values indicated in later sections of this paper.

TABLE 6.—Variation of Permeability with Temperature

A. PERMEABILITY TO CARBON DIOXIDE

| Sample No. | Permeability at 25° C | Temperature of test | Permeability at t° | Sample No. | Permeability at 25° C | Temperature of test | Permeability at t° |
|------------|--|---------------------|--|------------|--|---------------------|--|
| | Liters per m ² per 24 hours | t° | Liters per m ² per 24 hours | | Liters per m ² per 24 hours | t° | Liters per m ² per 24 hours |
| 1..... | 26.7 | 0.8 | 8.56 | 6..... | 26.7 | 80.0 | 113.3 |
| 2..... | 26.4 | 55.0 | 72.9 | 7..... | 28.6 | 98.3 | 146.2 |
| 3..... | 28.0 | 55.0 | 74.2 | 8..... | 27.4 | 98.5 | 142.4 |
| 4..... | 27.5 | 55.0 | 73.1 | 9..... | 27.4 | 98.8 | 145.4 |
| 5..... | 29.0 | 80.0 | 115.5 | | | | |

B. PERMEABILITY TO HYDROGEN

| | | | | | | | |
|--------|-------|------|------|--------|-------|------|------|
| 1..... | 9.30 | 1.9 | 3.51 | 5..... | 11.53 | 90.0 | 68.5 |
| 2..... | 9.86 | 2.8 | 3.79 | 6..... | 11.46 | 90.8 | 69.2 |
| 3..... | 10.45 | 70.0 | 44.8 | 7..... | 10.67 | 97.8 | 79.9 |
| 4..... | 11.50 | 70.0 | 46.1 | | | | |

C. PERMEABILITY TO HELIUM

| | | | | | | | |
|--------|------|------|------|--------|------|------|------|
| 1..... | 6.25 | 0.6 | 2.29 | 5..... | 6.51 | 90.0 | 37.0 |
| 2..... | 5.76 | .8 | 2.37 | 6..... | 6.43 | 90.0 | 38.5 |
| 3..... | 6.34 | 70.0 | 24.2 | 7..... | 6.62 | 97.3 | 44.6 |
| 4..... | 6.05 | 70.0 | 24.1 | 8..... | 6.48 | 97.6 | 44.4 |

It will be noted that the curves for hydrogen and helium show about the same relative increase with temperature. The change of permeability to carbon dioxide, however, becomes practically linear after 30° C. No simple relation between permeability and temperature has been discovered. Although it is without physical significance, the following equation represents the variation of hydrogen permeability very closely for this sample:

$$\text{Permeability} = (3800 + 217t + 2.4t^2 + 0.038t^3) 10^{-3}.$$

VI. PERMEABILITY OF RUBBER TO VARIOUS GASES

1. PERMEABILITY OF RUBBER TO HYDROGEN

In determining the permeability of rubber to different gases it is preferable to refer the values to some standard rather than attempt to express the permeability in absolute units. In this work the permeability to hydrogen has been adopted as the standard rate, because hydrogen is so generally used for filling balloon envelopes and because the greatest part of our knowledge of the permeability of rubber to gases concerns hydrogen. Accord-

ingly, the permeability to hydrogen of any sample of rubber has been set equal to unity; its permeability to any other gas is given as the ratio of its permeability to that gas to its permeability to hydrogen. In order to secure the required precision, it has been necessary to determine the permeability of every test piece both to hydrogen and to the gas in question.

The hydrogen used in all this work was made in a Kipp generator from a very pure lot of zinc and from "C. P." hydrochloric acid. It was purified by passage over soda lime and anhydrous granular calcium chloride. Conclusive tests made in another connection on hydrogen generated in this way showed it to contain not more than 3 or 4 parts in 10 000 of impurity when the generator was properly swept out.⁷

It was found that the ratio of permeabilities for different gases with different samples of rubber was fairly constant—sufficiently so to make the results of interest and value. In all probability the ratio varies somewhat with different samples of rubber; the extent of this variation is indicated roughly by the concordance of the results secured with different samples. In a preceding section a first approximation to the specific permeability of rubber to hydrogen was given; this value multiplied by the ratio of permeabilities of different gases will give approximately the specific permeabilities of those gases.

2. PERMEABILITY OF RUBBER TO OXYGEN

It is an interesting fact, first pointed out by Graham, that rubber is more permeable to oxygen than to nitrogen. As a result, air which has passed through rubber contains a higher percentage of oxygen than normal air. The significance of this fact in connection with the use of rubber-coated balloon fabrics has already been discussed in a report from this laboratory.⁸

The permeability of rubber to oxygen was determined with the apparatus of Fig. 1, with some appropriate minor changes. Air can not well be used as the comparison gas in the interferometer because its refractivity is not sufficiently different from that of oxygen, which fact gives rather low sensitivity. Hydrogen, however, differs greatly from air in refractivity and is therefore well adapted for this purpose. A current of oxygen was passed over one side of the fabric and hydrogen over the other side. The oxygen passing into the hydrogen was determined with the inter-

⁷ Edwards, Preparation and Testing of Hydrogen of High Purity, *J. Ind. Eng. Chem.*, **11**, p. 961; 1919.

⁸ Edwards and Ledig, "Significance of Oxygen in Balloon Gas," *Aviation and Aeronautical Eng.*, **6**, p. 325; 1919.

ferometer using hydrogen from the same source as the standard of comparison. The oxygen was analyzed volumetrically, using a burette with a constricted portion in which the unabsorbed residue could be measured quite accurately. Five analyses showed 99.50, 99.53, 99.55, 99.55, and 99.55 per cent oxygen. The results were corrected to a partial pressure of 100 per cent, using the value 99.55 as the existing partial pressure of oxygen.

The results of a series of tests are shown in Table 7. The average ratio of permeabilities, oxygen to hydrogen, is about 0.45. For this ratio Graham found the value 0.466 and Dewar's ⁹ curves show a value of 0.500 at 25° C.

TABLE 7.—Permeability of Rubber to Oxygen and Hydrogen

| Fabric No. | Permeability to oxygen | Permeability to hydrogen | Ratio of per- meabilities, oxygen to hy- drogen |
|------------|---|---|--|
| | Liters per m ² per 24 hours | Liters per m ² per 24 hours | |
| 50313..... | 5.09 | 11.83 | 0.430 |
| 50313..... | 5.16 | 11.91 | .433 |
| 50313..... | 4.84 | 10.81 | .448 |
| 50313..... | 4.97 | 10.77 | .461 |
| 50313..... | 4.82 | 11.06 | .435 |
| 50313..... | 5.30 | 11.52 | .460 |

Average ratio of permeabilities, oxygen to hydrogen, 0.445.

3. PERMEABILITY OF RUBBER TO NITROGEN

The permeability of rubber to nitrogen was determined in the same way as the permeability to oxygen except that nitrogen was used in place of oxygen. The results of these experiments are given in Table 8; the average ratio of permeabilities, nitrogen to hydrogen, is 0.16. Graham ¹⁰ gives the value 0.18 and Dewar's ¹¹ value is 0.12 (at 15° C).

TABLE 8.—Permeability of Rubber to Nitrogen and Hydrogen

| Fabric No. | Permeability to nitrogen | Permeability to hydrogen | Ratio of per- meabilities, nitrogen to hy- drogen |
|------------|---|---|--|
| | Liters per m ² per 24 hours | Liters per m ² per 24 hours | |
| 50313..... | 1.48 | 8.77 | 0.169 |
| 50313..... | 1.53 | 9.47 | .162 |
| 50313..... | 1.45 | 9.14 | .159 |
| 50313..... | 1.38 | 9.10 | .152 |
| 50313..... | 1.51 | 8.76 | .172 |
| 50313..... | 1.27 | 9.08 | .140 |
| 50313..... | 1.44 | 9.41 | .153 |
| 50313..... | 1.52 | 8.73 | .174 |

Average ratio of permeabilities, nitrogen to hydrogen, 0.160.

⁹ Proc. Roy. Inst., 21, p. 813; 1915.

¹⁰ Loc. cit.

¹¹ Loc. cit.

4. PERMEABILITY OF RUBBER TO ARGON

No experiments with argon were made in the course of the present work because a satisfactory sample of argon was not available. For the sake of completeness reference will be made to the work of Dewar¹² and of Rayleigh¹³ with argon. Dewar found the ratio of the permeabilities to argon and to hydrogen to be $\left(\frac{1.28}{5.6}\right) = 0.23$ at 15° C. Rayleigh found that in a sample of "air" which had diffused through rubber there was 1.93 per cent argon in the nitrogen after removing the oxygen. Atmospheric nitrogen contains $\left(\frac{0.94}{78.12}\right) = 1.23$ per cent argon. He therefore concluded that rubber was somewhat more permeable to argon than to nitrogen. The ratio of permeabilities, argon to nitrogen, calculated from his original data, is 1.6. Using the value we have found for the ratio nitrogen to hydrogen, the ratio argon to hydrogen would be 0.26.

5. PERMEABILITY OF RUBBER TO AIR

The permeability of rubber to air can be calculated from its permeability to oxygen and nitrogen by means of the proportionality between permeability and partial pressure. According to Sir William Ramsay the composition of air is as follows: Nitrogen, 78.12 per cent; oxygen, 20.94 per cent; and argon, 0.94 per cent. The permeability of rubber to air (referred to hydrogen) would then be

$$P = (0.7812 \times 0.16) + (0.2094 \times 0.45) + (0.0094 \times 0.26) = 0.22.$$

In confirmation of this value, the permeability to air was determined directly by the same method used in the case of oxygen and nitrogen. The refractivity of the air which had diffused through the rubber was calculated from the composition as determined by typical analyses. The influence of any probable variation in composition is negligible. The results are given in Table 9. Though the data are few in number and not very concordant, the average ratio, 0.23, is in close agreement with the value (0.22) which was just calculated.

¹² Loc. cit.¹³ Phil., Mag., 49, p. 220; 1900.

TABLE 9.—Permeability of Rubber to Air and Hydrogen

| Fabric No. | Permeability to air | Permeability to hydrogen | Ratio of permeabilities, air to hydrogen |
|------------|---|---|---|
| | Liters per m ² per 24 hours | Liters per m ² per 24 hours | |
| 50313..... | 2.21 | 9.45 | 0.234 |
| 50313..... | 2.14 | 8.73 | .245 |
| 50313..... | 1.97 | 9.40 | .210 |

Average ratio of permeabilities, air to hydrogen, 0.230.

The composition of air which has diffused through rubber is a matter of interest. This may be calculated from the permeability to nitrogen, oxygen, and argon and their partial pressures. The composition thus calculated is as follows:

| | |
|---------------|----------|
| | Per cent |
| Nitrogen..... | 56.8 |
| Oxygen..... | 42.3 |
| Argon..... | .9 |
| | 100.0 |

Graham found as much as 41.6 per cent oxygen in air which had diffused through rubber; Edwards and Ledig¹⁴ found 41 per cent.

These facts are of obvious practical importance in many instances.

6. PERMEABILITY OF RUBBER TO CARBON DIOXIDE

In determining the permeability to carbon dioxide, the regular method with the interferometer was employed. The carbon dioxide was generated from marble and hydrochloric acid and passed over anhydrous sodium carbonate and calcium chloride. Volumetric analysis showed the presence of 99.9 per cent carbon dioxide. The results of a series of these tests are shown in Table 10. Each permeability value recorded in the table is the average of 3 to 6 separate observations on the same test piece.

TABLE 10.—Permeability of Rubber to Carbon Dioxide and Hydrogen

| Fabric No. | Permeability to carbon dioxide | Permeability to hydrogen | Ratio of permeabilities, carbon dioxide to hydrogen |
|-----------------|---|---|---|
| | Liters per m ² per 24 hours | Liters per m ² per 24 hours | |
| 50313..... | 27.3 | 9.6 | 2.84 |
| 50313..... | 28.6 | 9.7 | 2.95 |
| Dental dam..... | 42.4 | 14.0 | 3.03 |
| 26293..... | 27.0 | 9.2 | 2.94 |
| 26293..... | 26.6 | 9.5 | 2.80 |

Average ratio of permeabilities, carbon dioxide to hydrogen, 2.91.

¹⁴ Edwards and Ledig, Significance of Oxygen in Balloon Gas, Aviation and Aeronautical Eng., 6, p. 325; 1919.

The values obtained for the permeability of fabric No. 50313 to hydrogen and carbon dioxide in the partial pressure experiments recorded in a previous section may be used to obtain a value for this ratio, even though the determinations with hydrogen and carbon dioxide were not made with the same test pieces. The average of seven determinations with hydrogen was 9.71 liters and the average of seven determinations with carbon dioxide was 27.86; the ratio is 2.87, which is in substantial agreement with the ratio 2.91 found in Table 10. It may be concluded that rubber is approximately 2.9 times as permeable to carbon dioxide as to hydrogen.

Values found by other experimenters for this ratio are of interest. Graham¹⁵ gives 2.47 as the ratio (temperature not specified). Kayser¹⁶ gives equations for the variation of permeability with temperature; the ratio of the permeabilities of rubber to carbon dioxide and hydrogen at 25° C as calculated from these equations is 2.48. Dewar,¹⁷ using thin films of rubber under tension and having a thickness of about 0.01 mm, found a value of 2.5 for this ratio at 15° C. In another series of experiments at "ordinary temperatures" Dewar¹⁸ found for the same film a relative rate of $\left(\frac{30.0}{8.4}\right) = 2.8$. All of these values are lower than those found in the present work. It should be noted, however, that all three experimenters used a volume or pressure method for determining the gas penetrating the rubber. Furthermore, the information obtainable from the published articles is insufficient to enable one to say whether or not the data are on a basis strictly comparable with ours. It is certain the results were not obtained under the conditions maintained in the present work; that is, an equilibrium condition with a continuous stream of pure gas over one side of the fabric and a stream of dry air over the other side. There is also a constant difference of pressure between the two sides of the rubber equivalent to 30 mm of water; the total pressure on the air side is 760 mm of mercury. These conditions more nearly simulate the conditions of use than those employed in the tests just discussed.

7. PERMEABILITY OF RUBBER TO HELIUM

A knowledge of the permeability of rubber to helium is of great importance at the present time, because of the recent development by the United States Government of a supply of helium for

¹⁵ Phil. Mag., 32, p. 401; 1866.

¹⁶ Wied. Ann., 43, p. 544; 1891.

¹⁷ Proc. Roy. Inst., 21, p. 813; 1915.

¹⁸ Proc. Roy. Inst., 21, p. 559; 1915.

filling airships. The investigation at the Bureau of Standards of the permeability of balloon fabrics to helium was made for the Bureau of Steam Engineering of the Navy Department. The helium employed was furnished by that bureau and was contained in a steel cylinder under 1,800 pounds pressure. Its composition as determined by our analysis was as follows:

| | Per cent |
|---------------|----------|
| Helium..... | 94.6 |
| Nitrogen..... | 5.2 |
| Methane..... | 0.2 |
| | <hr/> |
| | 100.0 |

The methane in the gas was determined by combustion with oxygen. The density of the gas was then determined with the Edwards gas-density balance and the composition calculated on the assumption that the residue was nitrogen and helium. Oxygen was tested for and shown to be absent. To confirm the analysis, a direct determination of nitrogen was made by absorption with metallic calcium. This method showed approximately 5 per cent nitrogen. When the gas was examined spectroscopically, neon and argon were found to be either absent or present in such small amounts as to be masked by the other gases present. Accordingly, it is thought that no appreciable error was introduced by the assumption that the residue consisted of helium and nitrogen. The refractivity of the mixture as determined with a Zeiss-Rayleigh interferometer indicated an amount of helium within 0.3 per cent of the value shown by the above analysis.

The amount of helium penetrating the fabric was determined with the interferometer in the usual way. Because of the large difference in the refractivities of air and helium $(2917-342) \times 10^{-7}$, the interferometer furnished a very sensitive means of determining helium. Each scale division indicated about 0.004 per cent helium in air; the total amount present could be determined with that precision.

The observed permeability obtained with the gas containing 94.6 per cent helium was corrected to the standard condition; that is, a difference in partial pressure of 100 per cent helium on the two sides of the fabric. This was done by multiplying the observed permeability by the ratio $\frac{100}{94.6-x}$ where x is the percentage of helium (usually about 0.4 per cent) on the "air side" of the fabric.

In Table 11 are given the permeabilities to helium and hydrogen of a number of samples of different fabrics. The fabrics tested are from three different manufacturers and include both envelope and ballonnet fabrics. Although there was considerable variation in the relative permeabilities, this variation could not be entirely ascribed to experimental error. It seems probable that part of this variation is due to differences in the relative permeabilities of different fabrics to these gases. The average ratio of 0.65 appears satisfactory for present purposes.

TABLE 11.—Permeability of Rubber to Helium and Hydrogen

| Fabric No. | Observed permeability to helium | Permeability corrected for 100 per cent helium | Observed permeability to hydrogen | Ratio of permeabilities, helium to hydrogen |
|------------|--|--|--|---|
| | Liters per m ² per 24 hours | Liters per m ² per 24 hours | Liters per m ² per 24 hours | |
| 27145..... | 9.6 | 10.2 | 16.1 | 0.63 |
| 45847..... | 9.8 | 10.3 | 15.7 | .66 |
| 45835..... | 7.6 | 8.0 | 14.0 | .57 |
| 35838..... | 7.4 | 7.9 | 13.7 | .58 |
| 36827..... | 6.4 | 6.8 | 10.0 | .68 |
| 36827..... | 6.7 | 7.0 | 10.6 | .66 |
| 36827..... | 6.5 | 6.9 | 10.7 | .64 |
| 36827..... | 6.2 | 6.6 | 10.0 | .66 |
| 36827..... | 6.6 | 7.0 | 10.6 | .66 |
| 36827..... | 6.1 | 6.4 | 9.5 | .67 |
| 36827..... | 6.3 | 6.7 | 9.3 | .72 |
| 36827..... | 6.5 | 6.9 | 9.4 | .73 |
| 36293..... | 5.7 | 6.1 | 9.8 | .62 |
| 24579..... | 4.8 | 5.1 | 8.7 | .59 |

Average ratio of permeabilities, helium to hydrogen, 0.65.

The other values for this ratio which appear in the literature are those of Dewar¹⁹ and Barr.²⁰ Dewar found a ratio of $\left(\frac{1.75}{5.6}\right) = 0.31$. No information is given regarding the helium used. Barr estimated the permeability to helium to be about two-thirds of the permeability to hydrogen, a value which is in agreement with ours.

8. PERMEABILITY OF RUBBER TO AMMONIA

Ammonia has been considered as a filling gas for balloons.

Its specific gravity is only 0.596, and it offers advantages from the standpoint of freedom from fire hazard and the fact that it can be transported in the liquid form. However, the fact that rubber is quite permeable to ammonia would necessitate the use of a different type of fabric for the balloon envelope.

¹⁹ Loc. cit.

²⁰ Barr British Advisory Comm. for Aeronautics, 1915.

In determining the permeability of rubber to ammonia it was necessary to use a special permeability cell made of steel, which would be unattacked by the ammonia. All connecting tubes coming in contact with the ammonia were either steel or glass. The ammonia which passed through the fabric into the air stream was absorbed in a measured volume of tenth-normal sulphuric acid and the excess acid determined by titration. Two small wash bottles were always used in series, but never more than a negligible amount of ammonia escaped absorption in the first wash bottle. Two sets of wash bottles were used, and they were connected to the cell alternately through a three-way cock. They were attached to the system by a mercury seal so that they could be easily detached. Each value recorded in the table is the average of a number of observations, each covering a half-hour period.

The ammonia was taken from a small steel cylinder, which had been evacuated to a very low pressure before filling with liquid ammonia. The gas can be considered to be free from air and water vapor; in fact, the total amount of impurity in this sample, which was carefully purified by fractionation, was shown by tests of C. S. Taylor, of this Bureau, to be less than 1 part per 100 000. The results of a series of experiments are given in Table 12. It was noted that it took considerable time to remove all the ammonia from the rubber, so that it was necessary to determine the permeability to hydrogen first in each case. The average ratio of the permeability to ammonia and hydrogen is probably very close to 8.

TABLE 12.—Permeability of Rubber to Ammonia and Hydrogen

| Fabric No. | Permeability to ammonia | Permeability to hydrogen | Ratio of permeabilities, ammonia to hydrogen |
|-----------------|--|--|--|
| | Liters per m ² per 24 hours | Liters per m ² per 24 hours | |
| 50313..... | <div> <div>71.9</div> <div>59.3</div> <div>61.1</div> </div> | 9.0 | 7.99 |
| 50313..... | <div> <div>71.8</div> <div>74.2</div> </div> | 9.1 | 8.02 |
| 50313..... | <div> <div>80.0</div> <div>80.9</div> </div> | 10.0 | 8.04 |
| Dental dam..... | <div> <div>119.6</div> <div>119.8</div> </div> | <div> <div>15.4</div> <div>14.8</div> </div> | 7.93 |

Average ratio of permeabilities, ammonia to hydrogen, 8.

^a These two results which were obtained on two succeeding days indicated that some change had occurred in the sample, and they are omitted from the average.

9. PERMEABILITY OF RUBBER TO ETHYL CHLORIDE

The permeability of rubber to ethyl chloride (C_2H_5Cl) is principally of interest because of the high value found and its relation to their mutual solubility. An interferometer of the portable type was used for determining the percentage of ethyl chloride passing through the fabric into the air stream. The interferometer was calibrated by the method previously referred to; for the purposes of this calibration the refractivity of ethyl-chloride vapor was calculated from values for the refractive index of the saturated vapor as recently determined at this Bureau. In making this calculation the refractivity of ethyl-chloride vapor at the partial pressures at which it was measured (4 to 5 per cent) was estimated from the density, which was calculated by means of Berthelot's equation of state. In doing this it was assumed that the partial pressure of the ethyl-chloride vapor in air followed Dalton's law.

The ethyl chloride was contained in a glass flask fitted with a steel valve, and the vapor could be readily withdrawn under its own pressure. It was prepared by C. S. Taylor, of this Bureau, from very pure materials and further purified by fractionation. The total impurity in the vapor phase was undoubtedly less than 1 part in 10 000, a purity far beyond that required for the present work.

TABLE 13.—Permeability to Ethyl Chloride and to Hydrogen

| Fabric No. | Permeability to ethyl chloride | Permeability to hydrogen | Ratio of permeabilities, ethyl chloride to hydrogen |
|------------|---|---|--|
| | Liters per m ² per 24 hours | Liters per m ² per 24 hours | |
| 50313..... | 1717 | 8.80 | 195 |
| 50313..... | 1851 | 9.76 | 190 |
| 50313..... | 1819 | 8.31 | 218 |
| 50313..... | 1763 | 9.44 | 187 |

Average rates of permeabilities, ethyl chloride to hydrogen, 198.

The permeability of rubber to ethyl chloride as shown by these few tests is approximately 190 to 200 times its permeability to hydrogen.

10. PERMEABILITY OF RUBBER TO METHYL CHLORIDE

For the purpose of comparison with ethyl chloride, the permeability of rubber to methyl chloride (CH_3Cl) was also determined. The interferometer was employed in estimating the percentage of methyl chloride in the same manner as with ethyl chloride. The only available data on the refractivity of methyl chloride are those of Mascart (N_D , 0° C, 760 mm = 1.000870);²¹ the calibration

²¹ From Landolt-Börnstein Phys. Tabellen.

is based on this value. The sample of methyl chloride used had been carefully purified by fractionation by C. S. Taylor. Three tests were also made with a sample of methyl chloride, the purity of which was unknown. These gave a ratio of permeabilities, methyl chloride to hydrogen, of 16.8, 17.6, and 17.8, but they are not included in the average. The other results are given in Table 14. The permeability of rubber to methyl chloride is approximately 18.5 times its permeability to hydrogen.

TABLE 14.—Permeability of Rubber to Methyl Chloride and Hydrogen

| Fabric No. | Permeability to methyl chloride | Permeability to hydrogen | Ratio of permeabilities, methyl chloride to hydrogen |
|------------|---|---|---|
| | Liters per m ² per 24 hours | Liters per m ² per 24 hours | |
| 50313..... | 173.8 | 9.43 | 18.4 |
| 50313..... | 185.8 | 9.58 | 19.4 |
| 50313..... | 174.8 | 9.68 | 18.1 |
| 50313..... | 180.3 | 9.86 | 18.3 |

Average rates of permeabilities, methyl chloride to hydrogen, 18.5.

11. PERMEABILITY OF RUBBER TO WATER VAPOR

The permeability of rubber to water vapor is interesting for a number of reasons. In view of the popular conception of rubber as a "waterproof" material, it might be thought that it was quite impermeable to water vapor, whereas the opposite is true—its permeability is relatively high. This fact is of great importance in many instances where rubber is used as a gas container; such as, for example, the use of rubber tubing in chemical and physical work. The use of rubber connections in any apparatus where the water content of the gas is important may introduce more or less serious errors.

The high permeability of rubber to water vapor renders its determination rather difficult. The first method employed in its determination was to pass a current of air saturated with water vapor at a temperature slightly below 25° C over the fabric, which was maintained in the cell at 25° C. A stream of air, previously dried over phosphorus pentoxide, was passed over the other face of the fabric and thence through an absorption tube filled with phosphorus pentoxide in which the water vapor could be absorbed and weighed. The results were very erratic, probably because of the low partial pressure of the water vapor in the air (about 3 per cent) and the large effect on the difference in partial pressure produced by small variations in the rate of passage of the dry air. The results, however, are confirmatory of those secured by the following method:

A shallow, crystallizing dish, 8 cm in diameter, was partly filled with phosphorus pentoxide and the top closed by a sheet of rubber, such as dental dam, which was fastened at the edge with rubber cement. The dish was then placed in an atmosphere saturated with water vapor and the rate of increase in weight determined. The results are shown in Table 15; obviously they only give an approximate figure, and no claim of accuracy is made for them. Lack of time prevented carrying this phase of the work farther. In connection with this table and the succeeding one, attention should be called to the fact that the permeability to water vapor is calculated for the assumed case of a difference in partial pressure of water vapor of 760 mm. This is done to make the results comparable with the hydrogen value. In any test the partial pressure of water vapor was about 20 mm.

TABLE 15.—Permeability of Rubber to Water Vapor and Hydrogen

[Air saturated with water vapor in contact with rubber]

| Sample No. | Permeability to water vapor (100 per cent partial pressure) | Permeability to hydrogen | Ratio of per- meabilities, water vapor to hydrogen |
|------------------------------|---|---|---|
| | Liters per m ² per 24 hours | Liters per m ² per 24 hours | |
| A 17—Thickness, 0.18 mm..... | 953 | | |
| | 969 | | |
| | 1270 | | |
| | 1001 | | |
| | 1108 | | |
| | 978 | | |
| | 1130 | | |
| | 1174 | | |
| | 975 | | |
| | 920 | | |
| | 1021 | | |
| | 875 | | |
| | 970 | | |
| | 890 | | |
| | 1030 | | |
| | 1019 | | |
| | 1262 | | |
| | 1075 | | |
| Average..... | 1034 | 22.0 | 47.0 |
| A 19—Thickness, 0.25 mm..... | 905 | | |
| | 905 | | |
| | 726 | | |
| | 1118 | | |
| | 860 | | |
| | 765 | | |
| | 905 | | |
| | 930 | | |
| Average..... | 889 | 14.3 | 62.0 |

A few experiments were also made with liquid water in contact with the rubber film. In these tests instead of cementing the rubber to the dish containing the phosphorus pentoxide, the rubber was cemented to the top of another exactly similar dish from which the bottom had been removed. The edges of both dishes were ground plane. The dish with the rubber film across the bottom was partially filled with water and placed on top of the dish containing the phosphorus pentoxide. When it was desired to weigh the lower dish, the upper dish was replaced by a watch glass. The results of these tests are shown in Table 16. In calculating the results the partial pressure of water vapor used was that corresponding to the temperature of the water in contact with the rubber.

TABLE 16.—Permeability of Rubber to Water Vapor

[Liquid in contact with rubber]

| Sample No. | Permeability to water vapor | Permeability to hydrogen | Ratio of per- meabilities, water vapor to hydrogen |
|------------------------------|---|---|---|
| | Liters per m ² per 24 hours | Liters per m ² per 24 hours | |
| A-18—Thickness, 0.21 mm..... | 1526 | | |
| | 1700 | | |
| | 1846 | | |
| | 1918 | | |
| Average..... | 1748 | 18.4 | 95.0 |
| A-19—Thickness, 0.25 mm..... | 1510 | | |
| | 1752 | | |
| | 1740 | | |
| | 1581 | | |
| | 1638 | | |
| | 1712 | | |
| | 1562 | | |
| Average..... | 1642 | 14.3 | 115.0 |

According to these few tests, the permeability of rubber to water vapor is about 50 times the permeability to hydrogen when saturated air is in contact with the rubber and about 100 times when liquid water is in contact with the rubber. In these methods diffusion processes were depended on to bring the water vapor into contact with the rubber and from the rubber to the phosphorus pentoxide. This factor should tend to give low values. The accidental errors of handling and weighing would probably be in the opposite direction.

Dewar in the work previously cited found for very thin rubber films in contact with liquid water a value which is 29.1 times the rate for hydrogen, both being measured at 15° C. Dewar found under similar conditions with ethyl alcohol in contact with the rubber a ratio of 25.9 which is lower than the value for water.

According to Kahlenberg,²² if water and alcohol are separated by a rubber film, the alcohol passes through into the water faster than the water passes into the alcohol which indicates a higher permeability to alcohol than to water. If both investigators are correct, it is an interesting case of the modification of permeability by another substance.

The present authors²³ found that saturating rubber with carbon dioxide did not change its permeability to hydrogen, but then, of course, the total dissolved gas was lower than in the case of either water or alcohol. Further data on these effects would be of interest.

VII. THEORY OF PERMEABILITY

One object of this investigation was to establish, if possible, a quantitative relationship between the permeability of a film of rubber to any particular gas and the various factors on which it is dependent. Only the part of the program detailed in the preceding pages was completed, however, before it became necessary to discontinue the work.

A simple and satisfactory picture of the process is one of dynamic equilibrium, in which the gas is dissolved at one side of the rubber at a rate proportional to its solubility and partial pressure and diffuses through the rubber where it evaporates from the other side. The same process takes place in the opposite direction, so that the net transference of gas is proportional to the difference in the partial pressures at the two faces of the rubber. Because of the lack of data it is not feasible to analyze the relations between solubility and rate of diffusion through the rubber. The permeability in every case investigated increases rapidly with increase of temperature. According to Kayser,²⁴ the solubility of both carbon dioxide and hydrogen decreases with increase of temperature. If this be true, there must be a rapid decrease in the internal resistance of the rubber to the passage of the gas, because the ordinary temperature coefficient of gaseous diffusion is unable alone to account for the facts.

²² J. Phys. Chem., 10, p. 141; 1906.

²³ J. Ind. Eng. Chem., 11, p. 966; 1919.

²⁴ Wied. Ann. 43, p. 544; 1891.

A rough parallel, with notable exceptions, may be drawn between the permeability of rubber to different gases and to the boiling points of the gases. In general, the higher the boiling point of the gas the greater the rate at which it penetrates rubber. The specific chemical characteristics of the gas and of the rubber colloid determine, however, the solubility, rate of penetration, etc., and not enough is known of them at the present time to warrant further speculation. There are, however, many interesting fields of investigation opened by this work, and the results should be extremely useful in the many cases where the behavior of rubber in contact with gases is concerned.

VIII. SUMMARY

Certain of the factors which determine the permeability of rubber to gases have been investigated and the relative rates of penetration of a number of gases determined. The major findings may be summarized as follows:

1. The permeability of rubber compounds varies with the composition, as would be expected. The aging of rubber films is accompanied by a decrease in permeability; a similar decrease may be affected by overvulcanization. The rubber which shows a very low permeability for these reasons is usually very much deteriorated and frequently brittle, so that it is a disadvantage from the standpoint of gas tightness.

2. The permeability to any gas is found to be directly proportional to its partial pressure, provided the total pressure is constant. The variation of permeability with total pressure depends on the thickness of the rubber, the way in which it is supported, etc.

3. The permeability to hydrogen is inversely proportional to the thickness of the rubber. No other gas was tested in this respect.

4. The specific permeability to hydrogen at 25° C of vulcanized rubber similar to the grade known as dental dam is about 20×10^{-6} cc per minute. This value varies somewhat with the age and chemical characteristics of the rubber.

5. The temperature coefficient of permeability is quite high. For example, in the tests at 100° C the permeability to carbon dioxide or helium was about 17 times the rate at 0° C; the permeability to hydrogen was about 22 times as great at 100° as at 0° C.

6. The relative permeability of rubber to some common gases is shown in the following summary:

TABLE 17.—Relative Permeability of Rubber

| Gas | Relative permeability, hydrogen=1 | Gas | Relative permeability, hydrogen=1 |
|---------------|-----------------------------------|----------------------|-----------------------------------|
| Nitrogen..... | 0.16 | Hydrogen..... | 1.00 |
| Air..... | .22 | Carbon dioxide..... | 2.9 |
| Argon..... | .26 | Ammonia..... | 8.0 |
| Oxygen..... | .45 | Methyl chloride..... | 18.5 |
| Helium..... | .65 | Ethyl chloride..... | 200.0 |

7. The permeability of rubber to water vapor is high—approximately 50 times the permeability to hydrogen. This value not having been determined with any precision is not included in the table above.

Special acknowledgment is due the Goodyear Tire & Rubber Co. for the samples of rubber and fabric furnished to us in the course of this work. Many of these were especially constructed to meet our specifications. Their enthusiastic cooperation was of great assistance.

WASHINGTON, February 25, 1920.







LIBRARY OF CONGRESS



0 018 373 890 2